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Alkyltriphenylphosphonium Arenesulfonates: Synthesis and Structures

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Abstract—The reactions of equimolar amounts of alkyltriphenylphosphonium bromide with arenesulfonic acids in an aqueous-acetone solution afford alkyltriphenylphosphonium arenesulfonates $[Ph_3PCH_2OMe]$-$[OSO_2C_6H_3(OH\text{-}4)(COOH\text{-}3)]$ (**I**), $[Ph_3PCH_2CN][OSO_2C_6H_4(COOH)\text{-}2]$ (**II**), $[Ph_3PCH_2C(O)Me]$-$[OSO_2C_6H_4(COOH\text{-}2]$ (**III**), and $[Ph_3PCH_2C(O)Me][OSO_2Naft\text{-}1]$ (**IV**). According to the X-ray diffraction (XRD) data, the crystals of compounds **I**–**IV** have ionic structures with tetrahedral alkyltriphenylphosphonium cations (P–C 1.7820(19)–1.8330(20) Å, CPC 105.37(10)°–112.09(12)°) and arenesulfonate anions. The crystal of compound **I** contains hydrogen bonds (S=O···H–OC(O) 1.87 Å) linking the arenesulfonate anions into chains. The structural organization of the crystals of compounds **I**–**IV** is mainly formed due to numerous weak hydrogen bonds between the cations and anions, for instance, S=O···H–C_{Ar} (2.29–2.70 Å), C=O···H–C (2.48 and 2.59 Å), and N···H–C (2.62–2.68 Å).

Keywords: alkyltriphenylphosphonium arenesulfonate, synthesis, structure, XRD

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INTRODUCTION

Problems of the synthesis of organophosphorus compounds (OPC) are actively studied due to their chemical advantages and wide possibilities of practical use. For instance, OPC are used as plasticizers, insecticides, fungicides, defoliants, herbicides [1], important intermediates in synthetic chemistry, particularly, in the Wittig reaction [2], organocatalysts in asymmetric interphase catalysis [3], and reagents for *transmetallation* [4] and metathesis of σ bonds [5]. In the petrochemical industry, OPC are used as additives to oils and gasolines in order to improve their quality [6]. Tetraorganylphosphonium salts are of huge significance in the production of new materials, catalytic systems, and ionic liquids manifesting unique properties [7–9]. In addition, OPC are applied as antimicrobial and antifungal drugs with a high biological activity and a low toxicity [10–12].

The most popular method for the synthesis of phosphonium salts is the quaternization of the corresponding phosphine due to the reaction with an electrophile or Brönsted acid [13–16]. The synthesized tetraorganylphosphonium halides further serve as a source of cations in the synthesis of diverse compounds.

The synthesis of a number of tetraorganylphosphonium arenesulfonates from tetraorganylphosphonium halides and arenesulfonic acids was described [17–21]. Mild experimental conditions and high yields of the complexes are advantages of this one-pot method, but the synthesis of the tetraorganylphosphonium derivatives bearing functional groups in organic radicals at the phosphorus atom and tetraorganylphosphonium salts with complicated anions have not been studied earlier.

The synthesis of new alkyltriphenylphosphonium arenesulfonates $[Ph_3PCH_2OMe][OSO_2C_6H_3$-$(OH\text{-}4)(COOH\text{-}3)]$ (**I**), $[Ph_3PCH_2CN][OSO_2C_6H_4$-$(COOH)\text{-}2]$ (**II**), $[Ph_3PCH_2C(O)Me][OSO_2C_6H_4$-$(COOH\text{-}2)]$ (**III**), and $[Ph_3PCH_2C(O)Me]$-$[OSO_2Naft\text{-}1]$ (**IV**) is presented in this work. Specific features of these compounds were determined by XRD.

EXPERIMENTAL

Alkyltriphenylphosphonium bromides and arenesulfonic acids (Alfa Aesar, Merck) were used. Acetone (reagent grade) served as the solvent.

Alkyltriphenylphosphonium arenesulfonates were synthesized by the addition of an equimolar amount of arenesulfonic acid in acetone to an aqueous solution of alkyltriphenylphosphonium bromide. The reaction mixture was stirred for 10 min, and acetone was evaporated. After filtration and evaporation of water, compounds **I**–**IV** crystallize as colorless crystals from the remained aqueous solution.

Methoxymethyltriphenylphosphonium 3-carboxy-4-oxybenzenesulfonate (I), T_m = 162°C, 90% yield. IR (ν, cm^{-1}): 3026 w, 2965 w, 2833 w, 1651 s, 1601 m, 1558 w, 1485 m, 1439 s, 1344 w, 1339 w, 1315 m, 1231 vs, 1157 m, 1117 s, 1097 s, 1074 m, 1022 s, 997 w, 947 m, 922 w, 893 m, 800 m, 781 m, 745 s, 723 m, 710 w, 683 m, 587 s, 530 s, 500 s, 457 m, 418 w. For $C_{27}H_{25}O_7PS$ anal. calcd., %: C, 61.77; H, 4.77. Found, %: C, 61.68; H, 4.85.

Cyanomethyltriphenylphosphonium 2-carboxybenzenesulfonate (II), T_m = 159°C, 85% yield. IR (ν, cm^{-1}): 3059 w, 2920 m, 2880 m, 2573 s, 1705 vs, 1587 m, 1560 w, 1489 m, 1439 vs, 1420 m, 1341 w, 1292 s, 1252 m, 1234 s, 1186 w, 1161 m, 1136 m, 1115 s, 1072 s, 1007 s, 905 w, 847 s, 802 w, 748 vs, 723 s, 685 s, 644 w, 613 s, 573 m, 548 s, 496 s, 436 w, 419 w. For $C_{27}H_{22}NO_5PS$ anal. calcd., %: C, 64.35; H, 4.37. Found, %: C, 64.06; H, 4.27.

Acetylmethyltriphenylphosphonium 2-carboxybenzenesulfonate (III), T_{decomp} = 123°C, 87% yield. IR (ν, cm^{-1}): 3022 w, 2955 m, 2913 m, 1717 vs, 1587 m, 1566 w, 1485 m, 1439 vs, 1389 w, 1360 s, 1298 s, 1256 vs, 1179 s, 1163 w, 1136 m, 1111 s, 1074 s, 995 s, 833 m, 799 m, 748 s, 723 s, 691 s, 644 w, 619 vs, 569 s, 525 w, 507 s, 494 m, 446 m, 420 w. For $C_{28}H_{25}O_6PS$ anal. calcd., %: C, 66.55; H, 4.80. Found, %: C, 66.47; H, 4.87.

Acetylmethyltriphenylphosphonium 1-naphthalenesulfonate (IV), T_{decomp} = 202°C, 86% yield. IR (ν, cm^{-1}): 3088 w, 3053 m, 2897 m, 2860 m, 1719 vs, 1585 m, 1504 m, 1439 vs, 1362 vw, 1310 m, 1233 s, 1198 s, 1157 w, 1111 s, 1043 vs, 1022 w, 993 m, 972 w, 880 m, 849 m, 812 s, 791 s, 746 s, 718 m, 687 s, 642 w, 613 vs, 561 s, 505 s, 449 w, 418 w. For $C_{31}H_{27}O_4PS$ anal. calcd., %: C, 70.65; H, 5.13. Found, %: C, 70.52; H, 5.22.

IR spectra were recorded on a Shimadzu IRAffinity-1S FT-IR spectrometer in KBr pellets. Thermoanalytical studies were carried out on a Netzsch STA Jupiter 449F1 synchronous thermal analyzer with the S-type holder for TG/DSC. Corundum microcrucibles (80 μL), oxidative atmosphere (dry air), and a flow rate of 50 mL/min were used. Elemental analysis was conducted on a Euro EA3028-HT analyzer. XRD was carried out on a D8 QUEST automated four-circle diffractometer (Bruker, graphite monochromator) at 293 K. Data were collected and primarily processed, unit cell parameters were refined, an absorption correction was applied, and the structures were determined and refined using the described software [22–24]. The structures were determined by a direct method and refined by least squares in the anisotropic approximation for non-hydrogen atoms. The main crystallographic data and structure refinement results for compounds **I**–**IV** are listed in Table 1.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2173236 (**I**), 2177206 (**II**), 2162501 (**III**), and 2170203 (**IV**); deposit@ccdc.cam.ac.uk or http://www.ccdc. cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The reactions of alkyltriphenylphosphonium bromides containing different functional groups with arenesulfonic acids (molar ratio 1 : 1) were found to afford alkyltriphenylphosphonium arenesulfonates in the yield up to 90%.

$$\mathrm{AlkPh_3PBr + HOSO_2Ar \xrightarrow{Acetone/H_2O} AlkPh_3POSO_2Ar + HBr}$$

$$\mathrm{Alk = CH_2OMe,\quad Ar = C_6H_3(OH\text{-}4)(COOH\text{-}3)\ (\mathbf{I});}$$

$$\mathrm{Alk = CH_2CN,\quad Ar = C_6H_4(COOH\text{-}2)\ (\mathbf{II});}$$

$$\mathrm{Alk = CH_2C(O)Me,\quad Ar = C_6H_4(COOH\text{-}2)\ (\mathbf{III}),\quad Naft\text{-}1\ (\mathbf{IV}).}$$

Synthesized compounds **I**–**IV** represent colorless crystals highly soluble in aromatic hydrocarbons and polar solvents and on heating in water. The thermal analysis curves for samples **I**–**IV** have a simple profile with one endothermic peak.

According to the XRD data, the crystals of compounds **I**–**IV** consist of the isolated tetrahedral alkyltriphenylphosphonium cations and arenesulfonate anions (Figs. 1–4).

The anions in the crystals of compound **I** contain intramolecular O–H···O=C contacts between the hydrogen atom of the hydroxyl group and the carbonyl oxygen atom equal to 1.84 Å and strong interionic hydrogen bonds (S=O···H–OC(O) 1.87 Å) via which the arenesulfonate anions are structured to form chains between which the cations are arranged (Fig. 5).

In the crystals of compounds **II** and **III**, the carboxyl groups of the anions form intramolecular hydrogen bonds of the S=O···H–OC(O) type (distances H···O 1.75 and 1.76 Å in **II** and **III**, respectively). Owing to the functional groups in the alkyl substituents at the phosphorus atom, the cations in the crystals of compounds **I**–**III** are joined into dimers via

Table 1. Crystallographic data and experimental and structure refinement parameters for compounds **I**–**IV**

Parameter	Value			
	I	**II**	**III**	**IV**
Empirical formula				
FW	524.5	503.49	520.51	526.56
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a, Å	8.867(11)	8.483(8)	11.268(15)	9.767(14)
b, Å	10.750(18)	11.714(13)	13.959(20)	21.365(14)
c, Å	14.066(16)	13.326(18)	16.63(2)	12.928(8)
α, deg	69.77(6)	106.63(4)	90.00	90.00
β, deg	82.20(3)	105.63(5)	97.48(5)	91.29(2)
γ, deg	81.75(5)	90.64(4)	90.00	90.00
V, Å^3	1240(3)	1216(2)	2594(6)	2697(3)
Z	2	2	4	4
ρ_{calc}, g/cm^3	1.405	1.375	1.333	1.297
μ, mm^{-1}	0.241	0.238	0.227	0.214
F(000)	548.0	524.0	1088.0	1104.0
Crystal size, mm	0.52 × 0.26 × 0.06	0.35 × 0.22 × 0.15	0.37 × 0.34 × 0.25	0.45 × 0.3 × 0.24
Range of data collection over 2θ, deg	5.84–58.26	6.48–56.8	5.5–57.1	6.3–56.94
Ranges of reflection indices	$-12 \le h \le 12$, $-14 \le k \le 14$, $-19 \le l \le 19$	$-11 \le h \le 11$, $-15 \le k \le 15$, $-17 \le l \le 17$	$-15 \le h \le 14$, $-18 \le k \le 18$, $-22 \le l \le 22$	$-13 \le h \le 13$, $-28 \le k \le 28$, $-17 \le l \le 17$
Measured reflections	45777	42510	62071	100779
Independent reflections (R_{int})	6640 (0.0457)	6029 (0.0360)	6487 (0.0532)	6785 (0.0440)
Refinement parameters	333	317	328	343
GOOF	1.020	1.018	1.127	1.025
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0463$, $wR_2 = 0.1124$	$R_1 = 0.0369$, $wR_2 = 0.0942$	$R_1 = 0.0949$, $wR_2 = 0.2842$	$R_1 = 0.0505$, $wR_2 = 0.1288$
R factors for all reflections	$R_1 = 0.0677$, $wR_2 = 0.1238$	$R_1 = 0.0507$, $wR_2 = 0.1025$	$R_1 = 0.1120$, $wR_2 = 0.2941$	$R_1 = 0.0661$, $wR_2 = 0.1403$
Residual electron density (max/min), e/Å^3	0.41/–0.47	0.23/–0.39	0.91/–0.42	0.50/–0.46

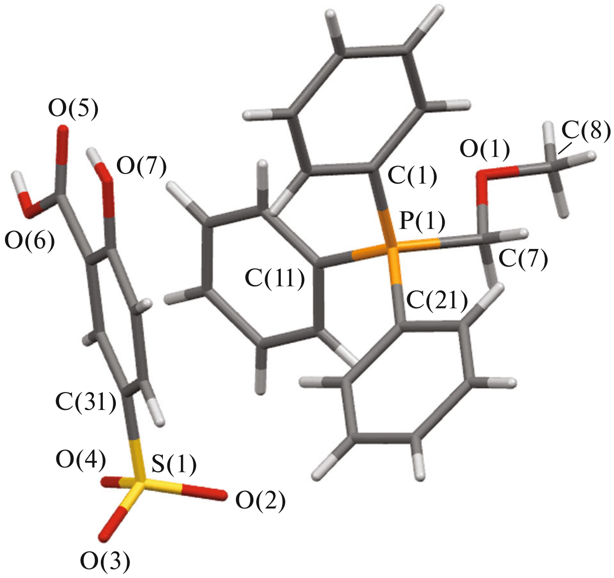

Fig. 1. General view of compound **I**. Bond lengths: P–C 1.790(2)–1.820(3), S–O 1.443(3)–1.464(2), and S–C 1.783(2) Å and bond angles: CPC 105.37(10)°–112.09(12)°, OSO 111.25(15)°–113.65(14)°, and OSC 105.81(12)–107.12(12)°.

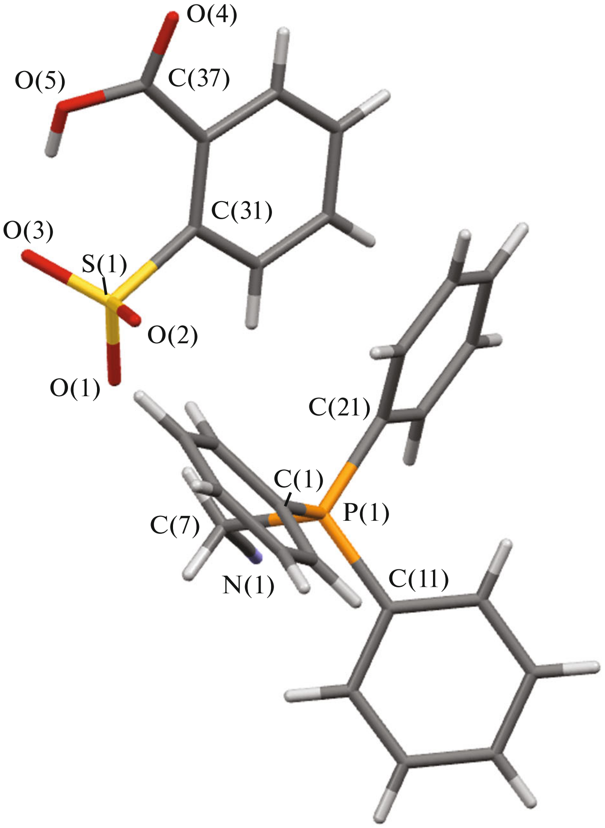

Fig. 2. General view of compound **II**. Bond lengths: P–C 1.785(2)–1.833(2), S–O 1.446(2)–1.464(2), and S–C 1.794(2) Å and bond angles: CPC 108.31(11)°–112.09(10)°, OSO 111.14(10)°–113.31(10)°, OSC 104.88(9)°–107.43(11)°.

weak O···H or N···H contacts: O(1)···H(14)–C(14) (2.53 Å) (**I**), O(1)···H(5)–C(5) (2.66 Å) (**III**), and N(3)···H(26)–C(26) (2.63 Å) (**II**). In compound **IV**, the cations form chains O(1)···H(14)–C(14) (2.57 Å) owing to these contacts. The structural organization of the crystals of compounds **I**–**IV** is mainly caused by numerous weak hydrogen bonds between the cations and anions, for example, S=O···H–C_{Ar} (2.29–2.70 Å), C=O···H–C (2.48 and 2.59 Å), and N···H–C (2.62–2.68 Å).

The IR spectra of compounds **I**–**IV** exhibit intense absorption bands in a range of 1110–1120 cm^{-1}, which is characteristic of the phosphonium salts containing at least one phenyl group bound to the phosphorus atom [25]. The ν(SO_2) vibrations in the sulfonate groups are characterized by the following frequencies: 1157, 1022 (**I**), 1136, 1072 (**II**), 1136, 1000 (**III**), and 1161, 1007 cm^{-1} (**IV**), which is consistent with the published data [26]. Very strong absorption bands at 1651 in **I**, 1705 in **II**, and 1717 cm^{-1} in **III** characterize stretching vibrations of the carbonyl groups. The IR spectra of compounds **I**–**IV** in a range of 3088–2860 cm^{-1} exhibit weak absorption bands corresponding to stretching vibrations of the C_{Me}–H and C_{Ar}–H bonds, and the IR spectrum of compound **II** also contains the band at 2573 cm^{-1} characteristic of the C≡N group [25].

To conclude, the reactions of equimolar amounts of alkyltriphenylphosphonium bromide and arenesulfonic acids in an aqueous-acetone solution af-forded new salts $[Ph_3PCH_2OMe][OSO_2C_6H_3(OH\text{-}4)(COOH\text{-}3)]$ (**I**), $[Ph_3PCH_2CN][OSO_2C_6H_4(COOH)\text{-}2]$ (**II**), $[Ph_3PCH_2C(O)Me][OSO_2C_6H_4$-

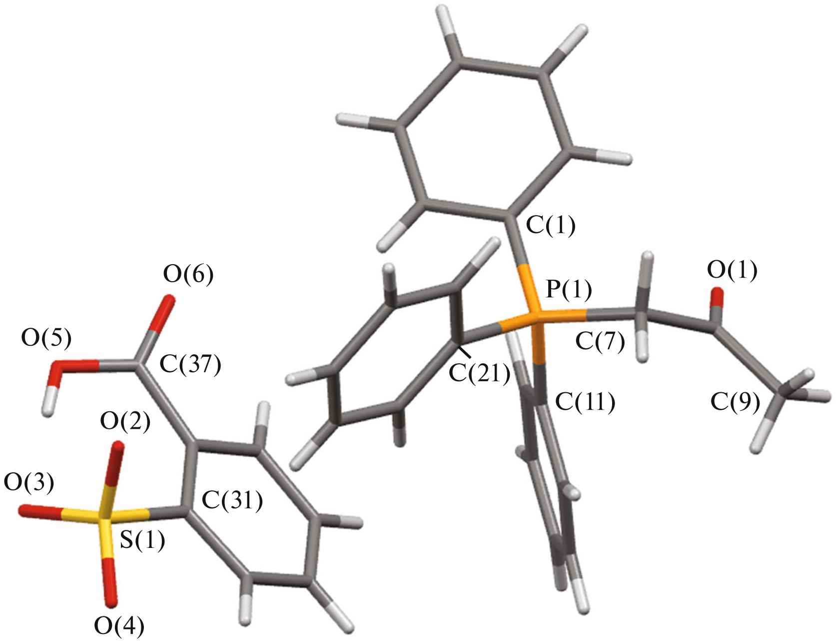

Fig. 3. General view of compound **III**. Bond lengths: P–C 1.784(5)–1.795(5), S–O 1.433(4)–1.457(5), and S–C 1.786(5) Å and bond angles: CPC 107.1(3)°–112.6(3)°, OSO 110.7(3)°–115.3(3)°, OSC 103.2(3)°–106.7(3)°.

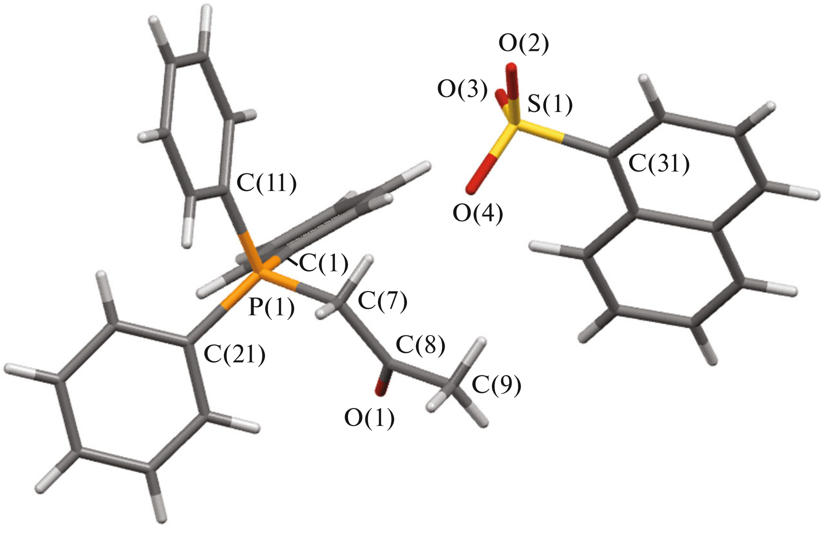

Fig. 4. General view of compound **IV**. Bond lengths: P–C 1.782(2)–1.796(2), S–O 1.433(2)–1.440(2) Å, and S–C 1.776(2) Å and bond angles: CPC 105.23(9)°–112.20(9)°, OSO 111.76(11)°–114.60(14)°, OSC 105.44(10)°–105.88(10)°.

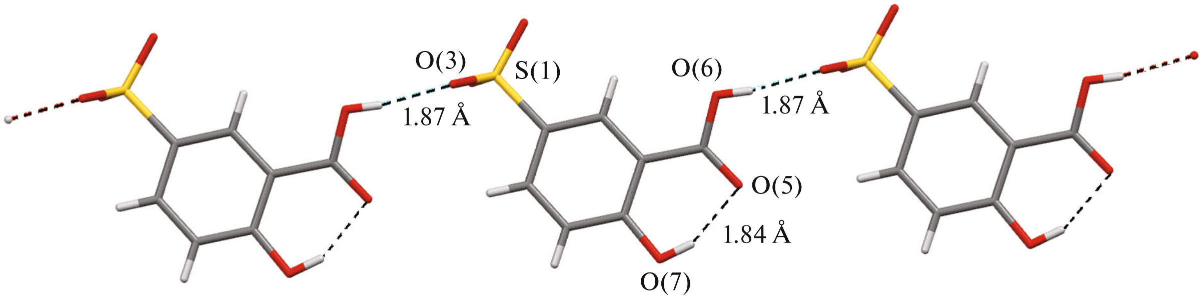

Fig. 5. Chain of the arenesulfonate anions in the crystal of compound **I**.

(COOH-2] (**III**), and $[Ph_3PCH_2C(O)Me]$-$[OSO_2$Naft-1] (**IV**). According to the XRD data, compounds **I**–**IV** have ionic structures with the tetrahedral alkyltriphenylphosphonium cations and arenesulfonate anions. The crystal of compound **I** contains strong hydrogen bonds (S=O···H–OC(O) 1.87 Å) via which the arenesulfonate anions are structured to form chains. The structural organization of the crystals of compounds **I**–**IV** is formed due to numerous weak hydrogen bonds between the cations and anions.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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